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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 341 859
A1**

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EUROPEAN PATENT APPLICATION

21 Application number: 89304162.4

51 Int. Cl.4: **G01N 27/30**

22 Date of filing: 26.04.89

30 Priority: 28.04.88 US 187175

43 Date of publication of application:
15.11.89 Bulletin 89/46

84 Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

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54 **Lithium ion-selective compositions, electrodes and a method of use.**

57 An analytical composition, electrode and method are useful for the detection of lithium ions in an aqueous liquid. The lithium ion-selective composition comprises a specific lipophilic group-substituted 1,10-phenanthroline, a compound capable of solvating the phenanthroline, and a supporting matrix. This composition can be used in a lithium ion-selective electrode as a lithium ion-selective membrane. The electrode can also comprise an internal reference electrode.

EP 0 341 859 A1

LITHIUM ION-SELECTIVE COMPOSITIONS, ELECTRODES AND A METHOD OF USE

This invention relates to clinical chemistry and particularly to lithium ion-selective compositions and electrodes. It also relates to methods of using the electrodes to potentiometrically determine lithium ions in aqueous liquids, for example, biological fluids.

In the diagnosis and treatment of various diseases as well as in preventative health care, it is important to monitor the concentrations of certain ions (for example cations) in a patient's body. One cation which has merited considerable attention in the treatment of patients suffering from manic-depressive psychosis is lithium ion. Other instances where monitoring the concentration of this ion is important is in the treatment of alcoholics.

One type of electrode useful for determining the concentration of various ions, such as lithium, potassium, sodium, calcium and other cations in a fluid is generally composed of a reference electrode of some type and an ion-selective membrane. The reference electrode is a half-cell which contributes to providing a detectable potential during an assay. The ion-selective membrane can be made of glass or a polymeric binder material and is impregnated with an ion-sensitive carrier and a solvent for the carrier. The ion-sensitive carrier, also known as an ionophore, is a compound which is capable of sequentially complexing the desired ion, and transporting it across the membrane interface.

A significant advance in the art is the dry-operative electrode described in U.S. Patent 4,214,968. The electrodes described therein have the advantage of providing reproducible potentiometric determinations of ion activity with no requirement for wet storage or preconditioning prior to use. This patent describes the electrodes as having a dried electrolyte layer comprising a solid salt dispersed in a hydrophilic binder. This electrolyte layer is also known in the art as a reference layer. Lithium ion-selective electrodes are described having cyclic polyethers as the ion carriers (Col. 16, lines 14-17).

Crown ethers have also been used as lithium ion carriers in lithium ion-selective membranes, as described for example by Kitazawa et al, Analyst, 110, pp. 295-299 (1985), and Kimura et al, J. Chem. Soc. Chem. Commun., pp. 669-700 (1985).

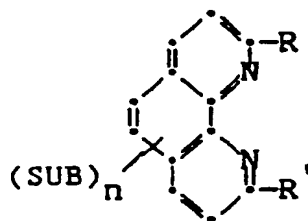
Phenanthrolines are known to complex and form coordination compounds with various cations, including alkali metal ions, alkaline earth metal ions and copper to name a few. For example, Pfeiffer et al (Zeitschrift für anorganische und allgemeine Chemie, 239, pp. 133-144, 1938) describe the preparation of lithium complexes with a perchlorate of o-phenanthroline. Also, an abstract of U.S.S.R. Patent 1,124,214 (published November 15, 1984) describes a magnesium ion-selective membrane composition comprising a complex of magnesium and a phenanthroline modified with a tetraphenyl borate (as the membrane active compound) and a carrier solvent. The magnesium-phenanthroline complex appears to be the matrix for the ion-selective borate compound. An abstract of U.S.S.R. 989,441 (published January 15, 1983) describes the use of bis-(2,9-dimethyl-1,10-phenanthroline)cupripicrate in a copper(I) ion-selective membrane and electrode.

U.S. Patent 3,483,112 describes an anion-selective electrode sensitive to perchlorate, halide, nitrate and other anions. The selectivity is allegedly obtained using an ion exchanger liquid comprising a salt of the anion and a metal (such as copper, iron or cobalt) complexed with an oleophilic group-substituted phenanthroline.

Lithium ion-selective compositions and electrodes are described by Sugihara et al (Chem. Letters, 12, pp. 2391-2392, December, 1987) wherein 2,9-dimethyl- and 2,9-di-n-butyl-1,10-phenanthrolines are used as ionophores. Research in this area continues to provide highly accurate assays for lithium ion which can be used in clinical environments with high confidence. There is a need for additional phenanthrolines which can be used with confidence in lithium ion-selective compositions and electrodes, particularly dry-operative electrodes and compositions useful therein.

The present invention provides a lithium ion-selective composition comprising a lipophilic group-substituted 1,10-phenanthroline, a compound capable of solvating the phenanthroline, and a supporting matrix,

the composition characterized wherein the phenanthroline has the formula (I):



wherein n is 0 to 6, R and R' are independently hydrogen or oleophilic monovalent organic groups, or one or both of R and R' form fused rings with the phenanthroline nucleus, or R and R' together form a macrocyclic ring attached to the phenanthroline nucleus, provided that both R and R' are not hydrogen, methyl or n -butyl unless n is greater than 0, and SUB represents an alkyl, aryl, cycloalkyl or halo.

The composition described above can be used as a dried lithium-ion selective membrane in a lithium ion-selective electrode. More particularly, a lithium ion-selective electrode comprises:

- (a) a reference electrode in contact with
- (b) a reference composition which is, in turn, in contact with one side of
- (c) the lithium ion-selective composition described above.

Further, a method for the potentiometric determination of lithium ions in an aqueous liquid comprises the steps of:

- A. contacting a sample of a fluid suspected of containing lithium ions with the membrane of the electrode described above.
- B. connecting the electrode to a second reference electrode, and
- C. detecting and comparing the electrical potentials generated by lithium ions in contact with the electrodes.

The present invention provides a composition, electrode and method useful for the determination of lithium ions in a highly accurate manner. In particular, the composition and electrode are highly selective for lithium ions in the presence of other cations, such as sodium, potassium and calcium. These advantages are achieved by using specific 1,10-phenanthroline compounds having one or more lipophilic substituents as lithium ion ionophores.

In general, the electrodes of the present invention are prepared using components and methods described in detail in U.S. Patent 4,214,968, noted above. Since most of the details are disclosed in that patent, the present disclosure will be directed to general summaries of the electrode components. As used herein, the terms "dry-operative" and "dried" have the meanings defined in U.S. Patent 4,214,968.

Thus, the term "dried" when used in reference to layers of electrodes described herein refers to a physical state of such layers brought about by subjecting, in manufacture, the layer to drying conditions, i.e. conditions for temperature, reduced vapor pressure or whatever, adequate to accomplish removal of sufficient solvent or dispensing medium as to render the layer non-tacky, as this term is commonly interpreted in the coating arts, prior to the application of any overlying layer(s). This drying to drive off solvent or dispensing medium is a major factor imparting the "dry-operative" capability to the electrodes of the present invention.

The term "dry-operative" describes an ion-selective electrode which provides reproducible potentiometric determination of ionic activity which can be related to the ion concentration of aqueous test solutions with no requirement for "wet" storage (i.e., keeping in an aqueous solution) or precondition (i.e., soaking in a salt solution) prior to use. Essentially, what this means is that a "dry-operative" electrode produces accurate and reproducible determinations of potential which can be calibrated and thereby related via ionic activity to ionic concentration in an aqueous test solution without having first to be substantially hydrated or brought to an equilibrium state. Many of the electrodes described herein perform in this manner even when used immediately after storage at 20% relative humidity.

The electrodes and devices of this invention can be used to determine the concentration of lithium ions in any aqueous liquid, including wastewater, cooling water, groundwater or food and brewery processing fluids. They are particularly useful for the assay of biological fluids, for example, blood sera and urine.

The electrode of the present invention can comprise an internal reference electrode which exhibits a reproducible reference potential against which the potential occurring at the interface between the ion-selective electrode and the solution under test is measured.

Generally, the reference electrode comprises a conductive metal layer of a suitable conductive metal

(for example, silver, mercury, platinum, nickel and the like). The conductive layer is in contact with a metal salt layer which may comprise substantially any insoluble salt of the metal in the conductive layer which establishes a fixed interfacial potential with the metal of the conductive layer. Preferably, the metal salt layer comprises a salt of the metal which is a product of oxidation of the metal, for example, a silver halide, or mercury halide. Such layers and techniques for making them are well known and described in more detail in U.S. Patent 4,214,968, noted above. Useful metal/metal salt electrodes include silver/silver halide and mercury/mercury chloride electrodes. Other useful reference electrodes are known in the art. A silver/silver halide reference electrode is preferred in the practice of this invention.

The lithium ion-selective electrodes of this invention can also comprise a dried electrolyte or reference layer in contact with the reference electrode. In one embodiment, the dried reference layer contains the dried residue of a salt and any optional addenda (surfactants or buffers), but is binderless (according to U.S. Patent 4,571,293).

According to a preferred embodiment, the reference layer is a dried hydrophilic layer comprising one or more dried hydrophilic binder materials, one or more salts uniformly distributed in the binder materials, and any optional addenda (such as surfactants or buffers). Preferably, the anion of one of the salts is common to the salt of the metal salt layer of the reference electrode, and at least a portion of the cation of the salt is lithium. The amounts and types of each component of the dried reference layer and the methods of preparation are readily determined by a skilled worker in the art in view of the teachings of U.S. Patent 4,214,968, noted above, and Japanese Patent Publication 58(1983)-102146.

The dried reference layer is in contact with a dry lithium-ion selective membrane composition. This composition is laminated, coated or otherwise applied directly over the reference layer.

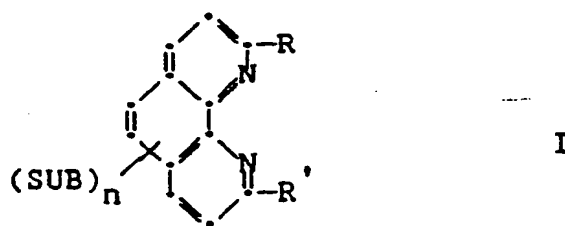
Generally, the composition of this invention comprises a 1,10-phenanthroline compound (described below) as an ionophore for lithium ions, a compound capable of solvating the ionophore (described below) and a supporting matrix comprised of one or more binder materials. The matrix can be any material which, in combination with the ionophore and solvating compound, is capable of forming a thin film of sufficient permeability to produce lithium ion mobility. Useful materials include porous glass, pressed fibers, and synthetic and natural polymeric materials, such as poly(vinyl chloride), carboxylated poly(vinyl chloride), poly(styrene-co-styrene sulfonic acid), poly(vinyl chloride-co-styrene sulfonic acid), poly(vinyl chloride-co-styrene carboxylic acid) and the like. Poly(vinyl chloride) is a preferred binder material in the practice of this invention.

The ionophore is solvated by one or more organic solvents which are capable of at least partially solvating the ionophore and providing lithium ion mobility. If a hydrophobic binder is used as the supporting matrix, the solvent must be compatible with the binder. The solvent is sometimes identified in the art as a carrier solvent. Useful carrier solvents include phthalates, sebacates, aromatic and aliphatic ethers, phosphates, mixed aromatic aliphatic phosphonates, adipates, nitrated ethers or esters or mixtures thereof, and others known in the art. Particularly useful solvents include, but are not limited to, dibutyl sebacate, bromophenyl phenyl ether, bis(2-ethylhexyl) sebacate, bis(2-ethylhexyl) 4-nitrophthalate, o-nitrophenyl valerate, dioctyl phenylphosphonate, o-nitrophenyl phenyl ether, o-nitrophenyl octyl ether, triisodecyl trimellitate, dimethyl phthalate, dilsodecyl phthalate, tris(2-ethylhexyl) phosphate, and mixtures thereof.

In addition, the composition of this invention can include one or more salts of oleophilic anions, such as a tetraaryl borate (for example, tetraphenyl borate). This salt can be present in amounts up to 33 mole percent based on the amount of 1,10-phenanthroline present, and preferably from 10 to 25 mole percent.

The composition can also comprise one or more surfactants and other optional addenda which do not interfere with lithium ion transport or selectivity.

The ionophores useful in the materials of this invention are oleophilic group-substituted 1,10-phenanthrolines. These phenanthrolines are substituted in at least one of the ring positions, and preferably they are substituted in at least one of the 2- and 9-positions of the ring, with at least one group or fused ring which contributes to the oleophilic nature of the compound and to complexing with a lithium ion. The compounds are insoluble in water and capable of being solvated by the carrier solvents described above. The phenanthrolines useful in this invention are used in uncomplexed form. In other words, they are not complexed to metal or other cations, or to anions. Generally, they are represented by the formula (I):



10 wherein R and R' are independently hydrogen or oleophilic monovalent organic groups, provided that both R and R' are not hydrogen, methyl or n-butyl unless n (defined below) is greater than 0. Useful organic groups include, but are not limited to, substituted or unsubstituted alkyl of 1 to 20 carbon atoms (such as methyl, ethyl, 2-chloroethyl, n-propyl, isopropyl, t-butyl, n-pentyl, 2-octyl, 2-ethylhexyl, methoxymethyl and dodecyl), substituted or unsubstituted cycloalkyl of 5 to 10 carbon atoms (such as cyclopentyl and

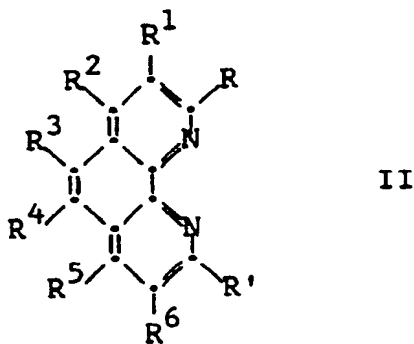
15 cyclohexyl), including bridged cycloalkyl groups, and cycloalkyl groups having side chains or side rings (such as bicyclo[3.1.0]hexane), substituted or unsubstituted aryl of 6 to 14 carbon atoms in the ring system, including fused ring systems [such as phenyl, naphthyl, 3,5-methoxyphenyl, 2-methoxy-3-(2-methoxyphenyl)phenyl, biphenyl and binaphthyl], and one or more alkyl, cycloalkyl or aryl as defined above which are interrupted with one or more oxy, thio or amino groups.

20 Also, one or both of R and R' can form a substituted or unsubstituted fused ring with the phenanthroline nucleus. Such fused rings can comprise from 3 to 5 carbon or hetero atoms in addition to those in the nucleus. Further, R and R' together can form a macrocyclic fused ring attached to the phenanthroline nucleus (such as catenanes or crown phenanthrolines).

25 In formula (I) above, SUB represents additional substituents which can be any of the alkyl, cycloalkyl or aryl groups defined above for R and R', or they can be halo groups (such as fluoro, chloro or bromo). Preferably, SUB is substituted or unsubstituted alkyl of 1 to 6 carbon atoms (as defined above) or substituted or unsubstituted aryl of 6 to 10 carbon atoms (as defined above). Also, n is from 0 to 6, but it is greater than 0 if both of R and R' are hydrogen, methyl or n-butyl.

30 In preferred embodiments, R and R' are independently substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, or substituted or unsubstituted aryl as defined above, SUB is substituted or unsubstituted alkyl or substituted or unsubstituted aryl as defined above, and n is 1 or 2.

Preferred substituted 1,10-phenanthrolines are represented by the structure (II):



wherein

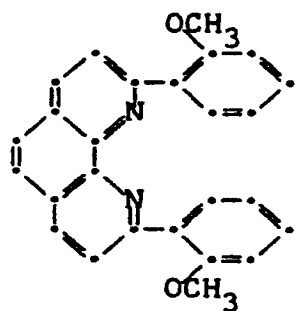
50 R is selected from the group consisting of substituted or unsubstituted alkyl having a molecular weight of at least 45, substituted or unsubstituted cycloalkyl having 5 to 10 carbon atoms in the ring and substituted phenyl,

R' is either hydrogen, halo or independently of R, selected from the groups defined for R,

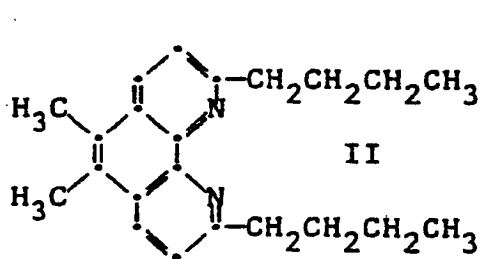
55 R¹, R², R³, R⁴, R⁵ and R⁶ are independently hydrogen, substituted or unsubstituted alkyl of 1 to 10 carbon atoms, substituted or unsubstituted cycloalkyl of 6 to 10 carbon atoms, substituted or unsubstituted aryl of 6 to 14 carbon atoms or halo groups,

provided that R' is not hydrogen when R is substituted or unsubstituted alkyl as defined above, and further provided that when R and R' are both either n-butyl-, t-butyl- or alkyl-substituted phenyl as defined above, at least one of R¹, R², R³, R⁴, R⁵ and R⁶ is alkyl, cycloalkyl, aryl or halo as defined above.

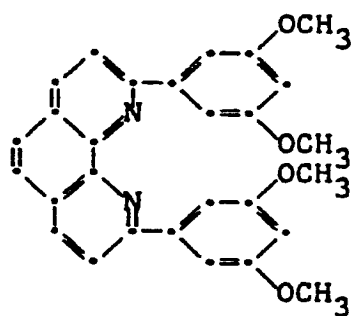
The following nonlimiting list shows representative phenanthrolines useful in the practice of this invention:



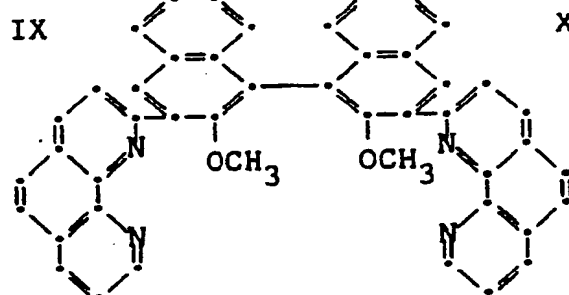
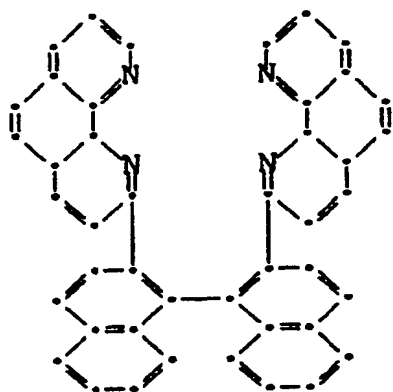
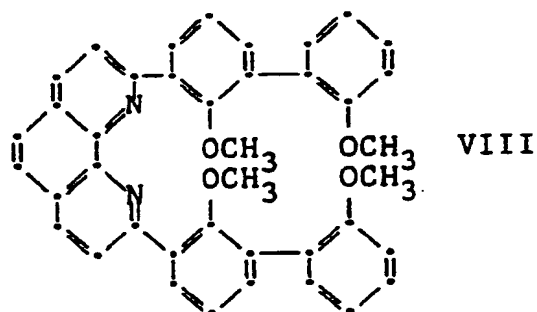
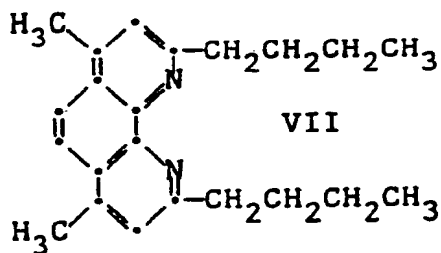
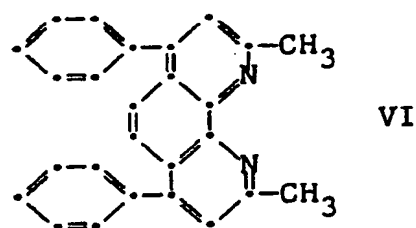
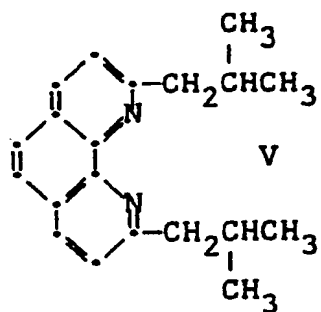
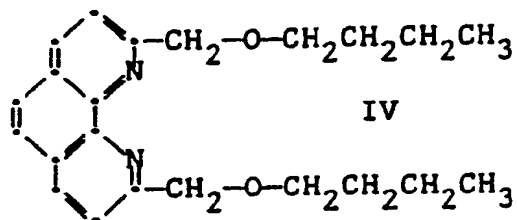
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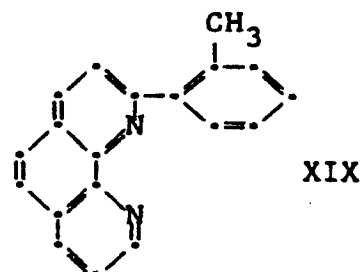
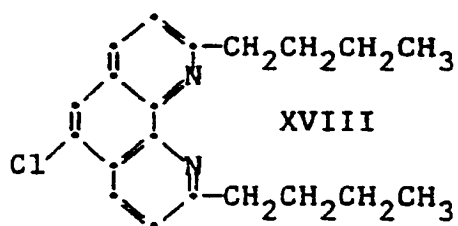
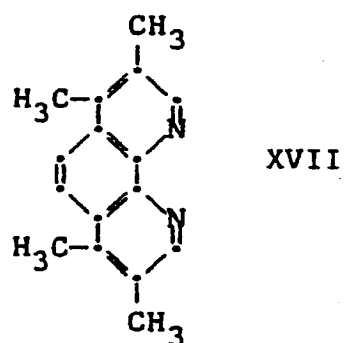
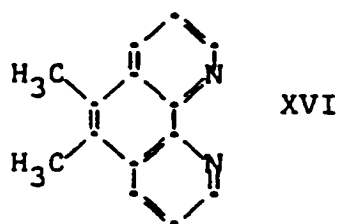
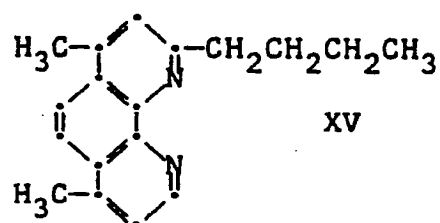
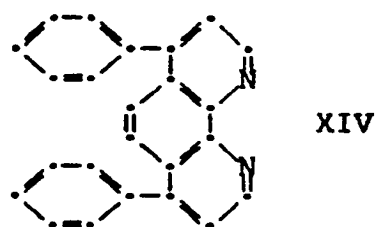
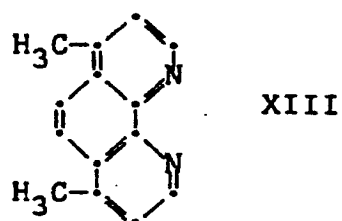
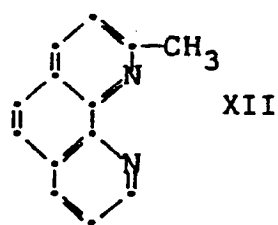
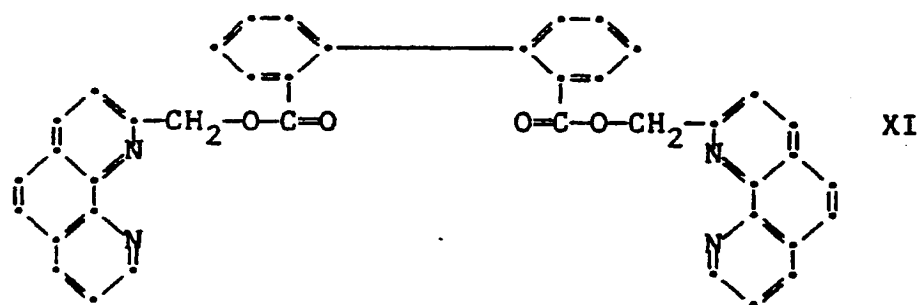


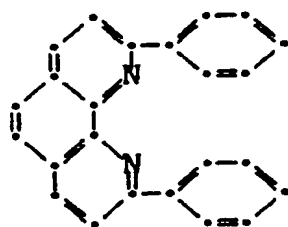
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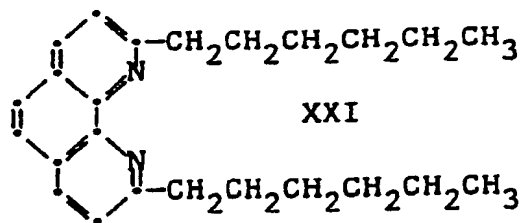
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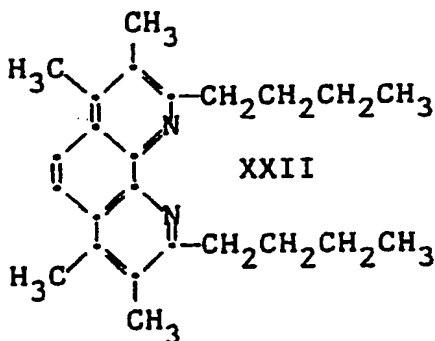




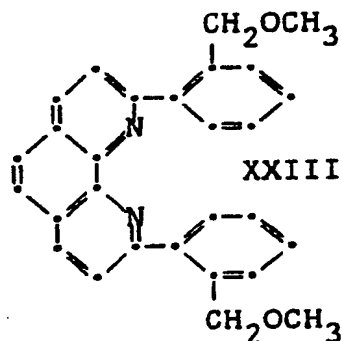
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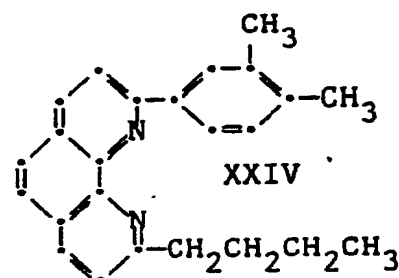
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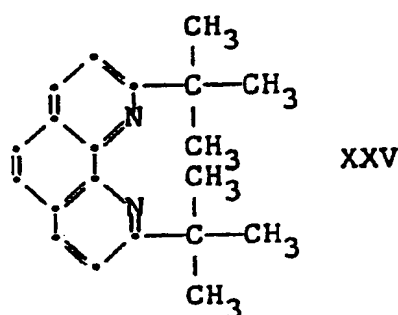
XXII



XXIII



XXIV



XXV

Of the compounds shown above, Compounds II, V, VII, XVIII, XXI and XXIV are preferred for use as lithium ionophores. Compounds II and VII are most preferred.

Some of the 1,10-phenanthroline compounds useful herein can be purchased from commercial sources, such as Aldrich Chemical and Eastman Kodak Co. Others can be prepared using known starting materials and procedures, as described herein and by Dietrich et al, *Tetra. Letters*, 5091, 1983. Other 1,10-phenanthrolines useful herein are prepared, as described below in the illustrated preparatory procedures.

In the membrane composition described above, generally, the 1,10-phenanthroline is present in an amount of from 0.1 to 1.5, and preferably from 0.2 to 0.8, g/m² of coated surface area. The amount of solvating compound will vary depending upon which solvent and phenanthroline are used, but generally, it is present in an amount sufficient to solvate the phenanthroline. Generally more solvent is used than is necessary to solvate the phenanthroline so that it remains solvated under a variety of storage conditions. A 100 to 500 percent excess on a weight basis is useful. Usually the amount of solvating compound is from 2 to 24 g/m².

The amount of supporting matrix which is present is determined by the desired thickness of the membrane and by the necessity for providing support for the phenanthroline-solvent dispersion. The membranes generally have a thickness in the range of from 2 to 20 μm. Generally, an amount of from 2 to 24 g/m² is useful.

Membranes including hydrophobic binder materials, an ionophore and solvating solvents are prepared using known film-coating or casting techniques. The amounts of each membrane component, including optional addenda, are described above and readily determined from the art.

The electrodes of this invention can be self-supporting, meaning that one or more layers of the electrode have sufficient mechanical strength to support the remaining portions of the electrode. Preferably, however, they further include a support which may be comprised of any material capable of bearing, either

directly or by virtue of some intervening adhesion-improving layer, the other necessary portions of the electrode described herein. The support may be porous or nonporous and be composed of wood, cellulose, ceramic, metal, glass, filter paper, polymeric or glass fibers or polymeric films. Preferably, the support is prepared from a nonporous polymeric film.

Lithium ion activity can be measured with the electrode of the present invention by measuring the steady-state difference in electrical potential between the fluid to be tested (test fluid) and a reference fluid in a cell arrangement schematically represented by the following:

Reference electrode 1/test fluid//membrane //reference fluid/reference electrode 2.

The calculations required to determine the ionic activity of the test fluid are derived from the well-known Nernst equation and are known to a skilled worker in the art.

The electrode of this invention incorporates within its structure substantially all of the components needed for making a potentiometric determination with the exception of a second reference electrode, a potential-indicating device (for example, an electrometer or potentiometer) and associated wiring. In use, the user merely contacts the membrane of the electrode with a sample of the test fluid (for example, less than 200 μ l) and connects the electrodes to a potential-indicating device. Contacting the fluid with the membrane can be done in any suitable manner, but preferably, a sample of the test fluid is applied to the membrane with a suitable dispensing means. Second reference electrodes for use in the assay, such as standard calomel electrodes, are well known. Similarly, electrometers are well known.

Alternatively and preferably, two or more electrodes of the present invention are incorporated or mounted into a frame to form a single device or test slide as it is sometimes known in the art. One of the electrodes is used to contact the test fluid while another is used as the second reference electrode to which the reference solution is contacted. Such a device is described in more detail in U.S. Patent 4,171,246. Such devices generally comprise a means for providing a liquid junction between the electrodes, including a capillary bridge formed of a strip of paper, a standard chromatographic strip, a strip of a porous polymeric film, natural or synthetic threads or fibers.

Preparation of 2,9-Di-n-butyl-5,6-dimethyl-1,10-phenanthroline (Compound II)

5,6-Dimethyl-1,10-phenanthroline monohydrate (0.83 g, 4.2 mmolar) was dissolved in 25 ml of freshly distilled tetrahydrofuran in a flask equipped for magnetic stirring and having an argon inlet. The contents were cooled in an iced water bath and n-butyl lithium (10 ml of 2.1 molar solution in hexane) was added dropwise with a syringe through a septum attached to the flask. An immediate color change to dark black-purple and then to bright yellow occurred upon addition of each drop of n-butyl lithium until about 2 ml had been added. Thereafter, the solution remained a dark purple color. When all of the n-butyl lithium had been added, the cold bath was removed and the reaction mixture allowed to warm to room temperature overnight.

After recooling the reaction mixture, it was quenched by the addition of methanol (a few ml) and then oxidized by the addition of a solution of iodine (9 g in 30 ml tetrahydrofuran) for 30 minutes. After an additional 60 minutes of stirring, the crude product was isolated by pouring the reaction mixture into saturated sodium bisulfite solution and extracting with a mixture of ethyl ether and dichloromethane. The extracts were washed sequentially with bisulfite solution, water and brine, and then dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure gave a dark oil which was purified by chromatography on silica gel using dichloromethane as eluant. In this manner, 0.7 g of the desired phenanthroline was obtained.

Examples 1-3: Lithium Ion-Selective Electrodes

These examples illustrate three lithium ion-selective electrodes of the present invention. Each electrode was prepared having the format and components shown below:

Membrane	Poly(vinyl chloride)	10	g/m ²
	o-nitrophenyl octyl ether	12	g/m ²
	1,10-Phenanthroline(see below)	0.5	g/m ²
	DC-510® silicone surfactant	0.06	g/m ²
Reference Layer (pH 4-8)	Gelatin	5	g/m ²
	Sodium chloride	2	g/m ²
	Lithium nitrate	0.5	g/m ²
	Surfactant 10G nonionic surfactant	0.06	g/m ²

The 1,10-phenanthroline compounds used in these electrodes are listed below:

- Example 1 Compound II
 Example 2 Compound V
 Example 3 Compound VII

Example 4: Determination of Lithium Ions

Several electrodes of this invention were used in the determination of lithium ions in an aqueous test solution. All of the electrodes were prepared as shown above in Examples 1-3.

The assays were carried out by applying a sample (5-25 μ l) of a test solution containing lithium ions and another cation (as a potential interferent) to the membrane of the electrode; and the electrochemical cell was completed with a suitable external reference electrode (a silver/silver chloride electrode). Selectivity coefficients were calculated using standard calculations from the difference in potential of the cell using a 0.1 molar solution of lithium chloride and an equimolar solution of the chloride of the other ion (that is, sodium, potassium or calcium).

A Control assay was similarly carried out using 2,9-di-n-butyl-1,10-phenanthroline as the ionophore.

Table I below shows the results of the assays and determination of selectivity coefficients. A coefficient less than 1.0 indicates selectivity of lithium ions over the other cations. The lower the coefficient, the better the lithium ion selectivity. It can be seen that some 1,10-phenanthroline compounds have high selectivity of lithium ions over all cations tested, whereas other compounds exhibit lithium ion selectivity over only one or two other cations.

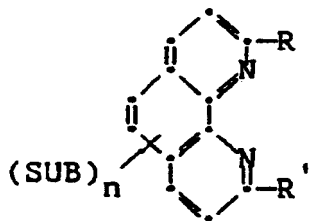
TABLE I

1,10-Phenanthroline Compound	Selectivity Coefficients		
	$k(\text{Li}^+/\text{Na}^+)$	$k(\text{Li}^+/\text{Ca}^{++})$	$k(\text{Li}^+/\text{K}^+)$
Control	0.0055	0.0071	0.0044
I	1.4	0.44	1.2
II	0.004	NT	NT
IV	0.98	0.052	0.064
V	0.0073	0.012	0.058
VI	0.12	0.071	0.10
VII	0.005	NT	NT
VIII	1.3	0.57	NT
IX	0.07	0.07	0.08
X	0.38	NT	NT
XI	0.22	0.064	0.33
XII	0.16	0.28	NT
XIII	0.08	0.16	0.046
XIV	0.05	0.05	0.02
XV	0.02	NT	NT
XVI	0.05	NT	NT
XVII	0.98	NT	NT
XVIII	0.025	NT	NT
XIX	0.14	NT	NT
XX	0.11	NT	NT
XXI	0.009	NT	NT
XXII	0.90	NT	NT
XXIII	0.058	0.00332	0.20
XXIV	0.019	NT	0.016

In Table I, "NT" means that the electrode was not tested for that particular selectivity coefficient.

Claims

1. A lithium ion-selective composition comprising a lipophilic group-substituted 1,10-phenanthroline, a compound capable of solvating the phenanthroline, and a supporting matrix, the composition characterized wherein the phenanthroline has the formula (I):

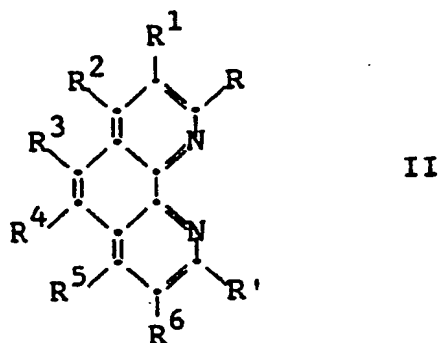


I

wherein n is 0 to 6, R and R' are independently hydrogen or oleophilic monovalent organic groups, or one or both of R and R' form fused rings with the phenanthroline nucleus, or R and R' together form a macrocyclic ring attached to the phenanthroline nucleus, provided that both R and R' are not hydrogen, methyl or n-butyl unless n is greater than 0, and SUB represents an alkyl, aryl, cycloalkyl or halo.

2. The composition as claimed in claim 1 wherein n is 1 or 2, R and R' are selected from the group consisting of alkyl of 1 to 20 carbon atoms, aryl of 6 to 14 carbon atoms, or cycloalkyl of 5 to 8 carbon atoms, and SUB is alkyl of 1 to 6 carbon atoms or aryl of 6 to 10 carbon atoms.

3. The composition as claimed in either of claims 1 or 2 wherein the phenanthroline has the structure (II):



wherein

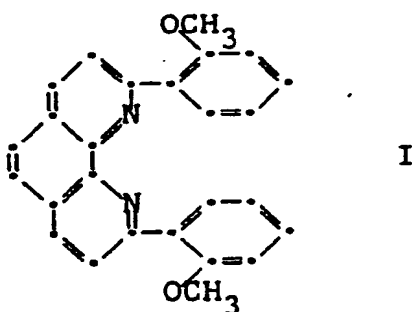
R is selected from the group consisting of alkyl having a molecular weight of at least 45, cycloalkyl having 5 to 14 carbon atoms in the ring and substituted phenyl,

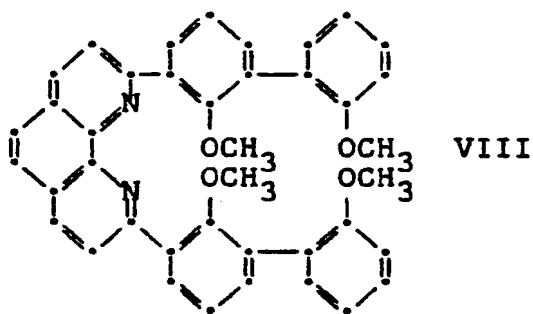
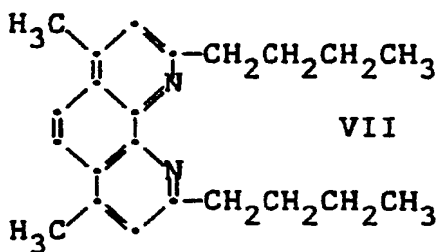
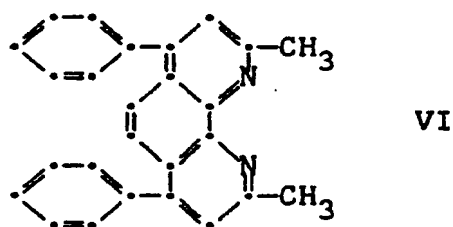
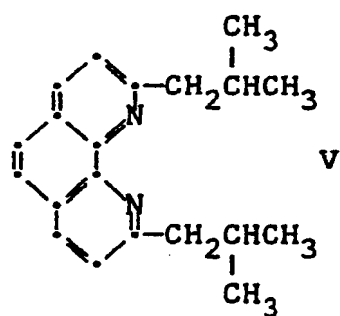
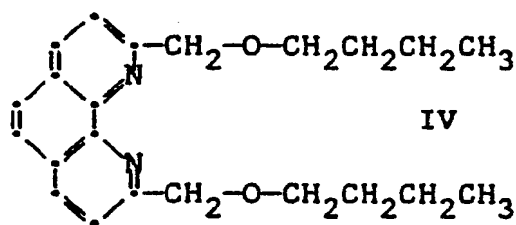
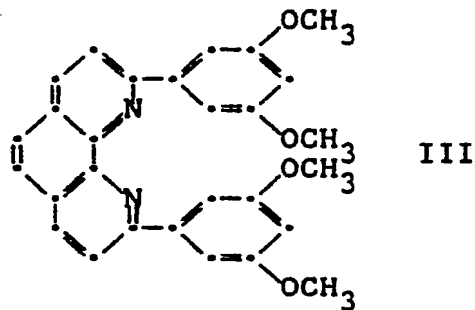
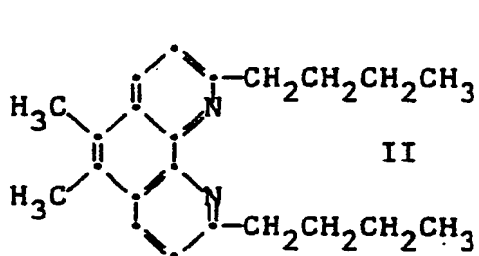
R' is either hydrogen, halo or independently of R, selected from the groups defined for R,

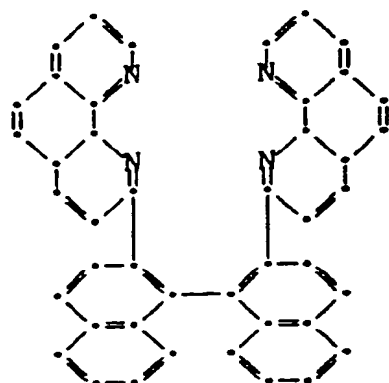
R¹, R², R³, R⁴, R⁵ and R⁶ are independently hydrogen, alkyl of 1 to 10 carbon atoms, cycloalkyl of 6 to 10 carbon atoms, aryl of 6 to 10 carbon atoms or halo groups,

provided that R' is not hydrogen when R is alkyl as defined above, and further provided that when R and R' are both either *n*-butyl-, *t*-butyl- or alkyl-substituted phenyl as defined above, at least one of R¹, R², R³, R⁴, R⁵ and R⁶ is alkyl, cycloalkyl, aryl or halo as defined above.

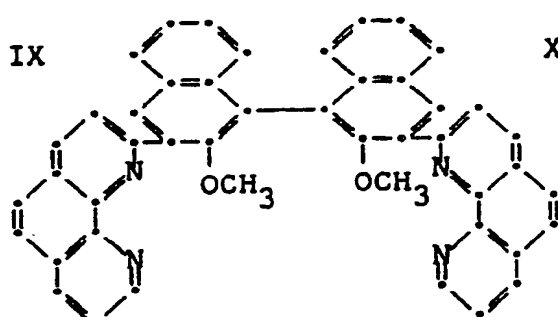
4. The composition as claimed in any of claims 1 to 3 wherein the phenanthroline is one of the following compounds:



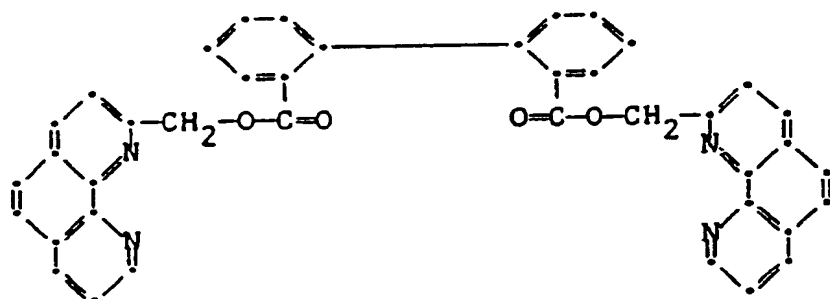




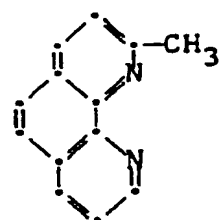
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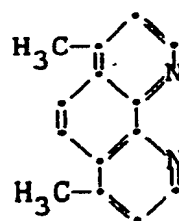
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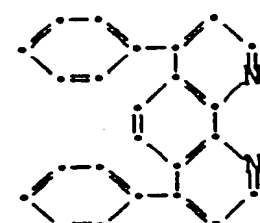
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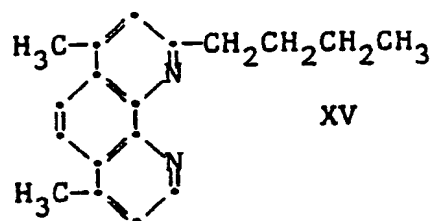
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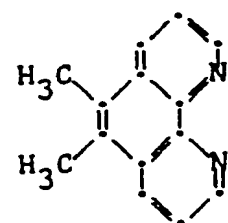
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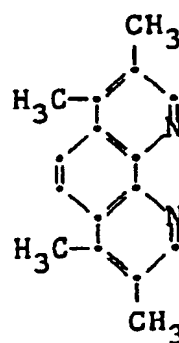
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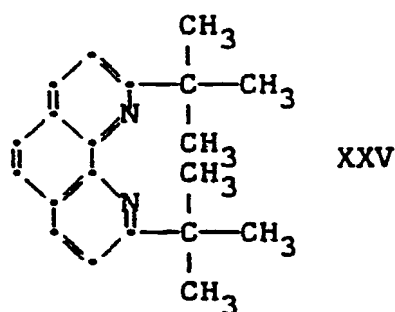
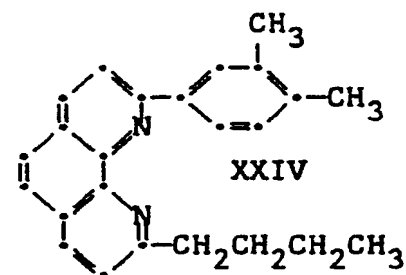
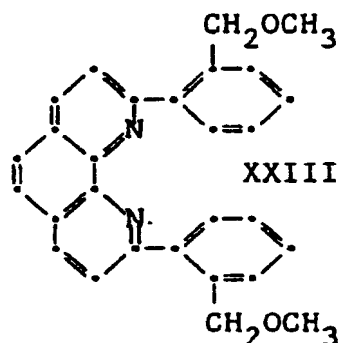
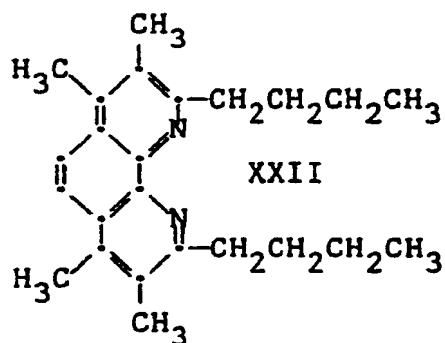
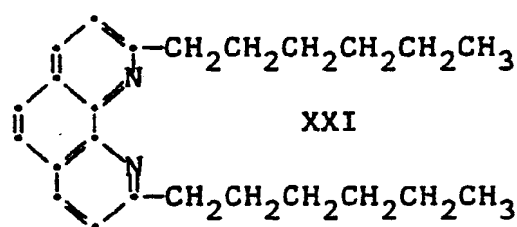
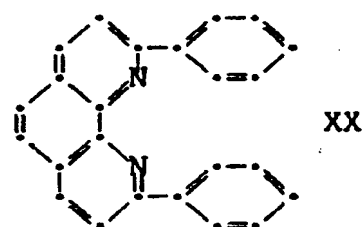
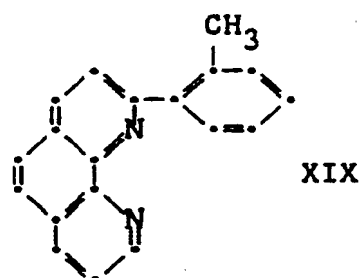
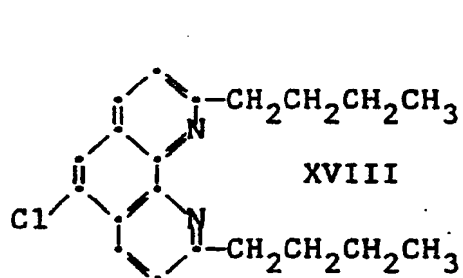
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XVI



XVII



5. The composition as claimed in any of claims 1 to 4 wherein the supporting matrix is a hydrophobic binder.

6. The composition as claimed in any of claims 1 to 5 wherein the hydrophobic binder is poly(vinyl chloride).

7. A lithium ion-selective electrode characterized as having a dried lithium ion-selective membrane prepared from the composition as claimed in any of claims 1 to 6.

8. A lithium ion-selective electrode comprising:

(a) a reference electrode in contact with

(b) a reference composition which is, in turn, in contact with one side of

(c) a dried lithium ion-selective composition as claimed in any of claims 1 to 6.

9. A dry-operative lithium ion-selective electrode comprising:

5 (a) a dried internal reference element comprising the dried residue of a solution of a salt and a hydrophilic polymeric binder in a solvent for the polymer and the salt and,

(b) in contact with the reference element, a hydrophobic lithium ion-selective membrane of predetermined uniform thickness in regions thereof intended for contact with a sample for analysis, the membrane prepared from the composition as claimed in any of claims 1 to 6.

10 10. A method for the potentiometric determination of lithium ions in an aqueous liquid comprising the steps of:

A. contacting a sample of a fluid suspected of containing lithium ions with the membrane of a lithium ion-selective electrode the membrane prepared from the composition as claimed in any of claims 1 to 6,

B. connecting the electrode to a second reference electrode, and

15 C. detecting and comparing the electrical potentials generated by lithium ions in contact with the electrodes.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,X	CHEMISTRY LETTERS, vol. 12, 1987, pages 2391-2392, The Chemical Society of Japan, JP; H. SUGIHARA et al.: "Lithium ion-selective electrodes based on 1,10-phenanthroline derivatives" * Abstract; table 1; figure *	1,5-7	G 01 N 27/30
D,A	IDEM ---	2,3	
D,A	TETRAHEDRON LETTERS, vol. 24, no. 46, 1983, pages 5091-5094, Pergamon Press Ltd, Oxford, GB; C.O. DIETRICH-BUCHECKER et al.: "Synthese de composés polyethers macrocycliques dérivés de la phenanthroline-1,10 diphenyl-2,9" * Figure 1 *	1,3	
D,A	US-A-3 483 112 (ROSS) * Column 2, line 60 - column 3, line 3; abstract *	1-4,8	
D,A	US-A-4 214 968 (BATTAGLIA) * Abstract; figure 1 *	8-10	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 01 N
D,A	ZEITSCHRIFT FÜR ANORGANISCHE UND ALGEMEINE CHEMIE, vol. 239, 1938, pages 133-144, Verlag Johann Ambrosius Barth, Leipzig, DE; P. PFEIFFER et al.: "Komplexsalze der Alkali-und Erdalkalimetalle" * Page 133, formulas *	1	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-08-1989	Examiner BOSMA R.A.P.
CATEGORY OF CITED DOCUMENTS			
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	ANALYTICAL CHEMISTRY, vol. 58, no. 9, August 1986, pages 1948-1953, American Chemical Society, Washington, DC, US; V.P.Y. GADZEKPO et al.: "Comparative study of neutral carriers in polymeric lithium ion selective electrodes" * Abstract; figure 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-08-1989	Examiner BOSMA R.A.P.
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